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### (54) Plastic container and method for manufacturing the same

Kunststoffbehälter und Verfahren zu seiner Herstellung

Récipient en matière plastique et procédé de fabrication

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EP-A- 0 118 227	EP-A- 0 199 564
EP-A- 0 204 324	FR-A- 2 207 806
FR-A- 2 383 091	

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## Description

The present invention relates to a container made of a laminated plastic sheet and a method for manufacturing the same. More particularly, the present invention pertains to a container having a gas-barrier characteristics and a method for manufacturing the same.

It is desirable that containers for foodstuffs are capable of protecting the contents therein so that the contents do not get adverse effects even after the contents have been handled for transportation and stored for an extended period of time under a room temperature, and that they are capable of being subjected to heating and cooking with a microwave oven. Further, those containers which are subjected to a retort sterilization have to be of a property which can withstand a high temperature and a high humidity to which the containers are subjected. Plastic material is preferred for manufacturing such containers because of the lower cost and readiness for the manufacture.

Conventionally, containers for foodstuffs have been manufactured by means of for example forming a sheet of a plastic material under an elevated temperature, a blow forming, or an injection molding. Since containers for foodstuffs must be harmless to the contents therein and are required to be capable of providing a barrier to liquid and gas which may penetrate from the inside of the container to the outside and to gas which may penetrate from the outside to the inside of the container, it is recommendable to manufacture the container from a laminated sheet made of a plurality of layers respectively having properties as required. A preferable method for the manufacture of the container is to form the sheet under an elevated temperature. Examples of such containers are disclosed in FR-A-2 207 806, EP-A-0 204 324, and EP-A-0 199 564.

Conventionally, such containers have been manufactured from a sheet of a plastic material such as polystyrene resin, ABS resin or polypropylene resin by forming the sheet under an elevated temperature. However, the conventional method cannot provide a container having a satisfactory gas barrier property so that the container manufactured through the conventional method has only a limited use. In order to provide a gas barrier property, it has been known to use a laminated sheet including a metal foil covered at the opposite sides by plastic layers such as layers of polypropylene layers and form the sheet into a desired configuration under an elevated temperature. The conventional method using such a laminated sheet is however limited to the manufacture of a container of a relatively shallow configuration such as a tray because of the metal foil contained in the laminated sheet. Therefore, it has not been possible to manufacture with this method a container of a deep configuration such as a cup, bowl and the like. It should further be noted that the container thus manufactured from the laminated sheet is not suitable for a cooking by a microwave oven.

It has been known that some kinds of polymer material such as vinylidene chloride copolymer, ethylene-vinyl alcohol copolymer has an improved gas barrier property when it is stretched. When such resin material is used for the manufacture of a container, the forming must be conducted with the resin material in a softened condition so that the stretched condition can be maintained. However, when a container is thus formed with the resin material in a softened condition, it cannot maintain its shape under a high temperature to which the container will be subjected when a hot content is to be charged or when the content is being subjected to a retort sterilization. As the result, the container may be distorted under such high temperature. If the forming is carried out with the resin material in a molten condition, it will no longer be possible to maintain the stretched condition of the material so that the property of the material cannot be utilized to provide an improved gas barrier property.

It is therefore an object of the present invention to provide a container which utilizes the property of a polymer material in which the gas barrier property can be improved under a stretched condition but in which the shape of the container can be maintained even under an elevated temperature.

Another object of the present invention is to provide a plastic container which has an improved gas barrier property but can maintain its shape even under an elevated temperature.

Still further object of the present invention is to provide a process for manufacturing such a plastic container.

According to the present invention, the above and other objects can be accomplished by a container including

an inner layer and an outer layer each made of a thermoplastic material selected from polypropylene resin, high density polyethylene resin, polyethylene-terephthalate resin, polycarbonate resin and polymethyl pentene resin, and

a barrier layer disposed between said inner and outer layers and made of a resin material, selected from vinylidene chloride copolymer, ethylene-vinyl alcohol copolymer, polybutylene-terephthalate, acrylonitrile copolymer, nylon-6, metaxylenediamine, and condensed adipic acid copolymer,

said barrier layer being held between the inner and outer layers with the resin material constituting the barrier layer being in a stretched condition and the thermoplastic material of said inner and outer layers being in a non-stretched condition.

Preferred embodiments of the invention are described in dependant claims 2-6.

Preferably, the inner and outer layers are made of polyolefin resin such as polypropylene or polyethylene. Polyester, polycarbonate and polymethylpentene may also be used. The barrier layer may preferably be made of stretched vinylidene chloride copolymer or stretched ethylene-vinyl alcohol copolymer. Acrylonitrile copoly-

mer, polybutylene-terephthalate, nylon-6, metaxylene-diamine and condensed adipic acid copolymer may be used. Further, the barrier layer may be of two-layer structure including a first barrier layer of, for example, stretched vinylidene chloride copolymer and a second barrier layer of, for example, stretched ethylene-vinyl alcohol copolymer. In this instance, it is preferred to arrange the first barrier layer at a side adjacent to the inner layer and the second barrier layer at a side adjacent to the outer layer. It is preferred to provide a rigid layer of a large thickness outside the outer layer. The rigid layer may preferably contain inorganic material. The outer surface of the rigid layer containing the inorganic material may preferably be coated with a coating layer of a thermoplastic resin.

The present invention further provides a method for manufacturing a container. The method in accordance with the present invention is characterized by steps of providing a laminated sheet including an inner layer made of a thermoplastic resin, an outer layer made of a thermoplastic resin and an intermediate layer made of a resin whose gas barrier property can be improved by stretching the resin, the intermediate layer being held between the inner and outer layers, and forming the laminated sheet into a configuration of the container under a temperature which is higher than the melting temperature of the inner and outer layers but lower than the melting temperature of the intermediate layer.

Where the inner and outer layers are maintained substantially the same in temperature with the barrier or intermediate layer during the forming process, it is necessary for the barrier layer to be made of a material which has a melting temperature higher than the melting temperature of the inner and outer layers. Where the heating process is carried out by applying heat outside the inner and outer layers to produce a temperature gradient between the inner and outer layers and the barrier layer, the material for the barrier layer may have a melting temperature which is substantially the same as that of the inner and outer layers because it is possible to maintain the barrier layer at a temperature in which the barrier layer can be stretched due to the temperature gradient.

In carrying out the method described above, it is preferable to proceed with the forming step after a rigid layer of a large thickness is provided outside the outer layer of the laminated sheet. According to a preferable mode of the present invention, the method is carried out by providing a laminated sheet comprising an inner layer made of a polypropylene film, an outer layer made of polypropylene film and an intermediate layer between the inner and outer layers and made of a film of vinylidene chloride copolymer, providing the outer side of said outer layer with a rigid layer containing organic material, forming the laminated sheet with the rigid layer into a desired shape under a temperature which is higher than the melting temperature of the inner and outer layers but lower than the melting temperature of the intermediate layer so that the vinylidene chloride

5 copolymer film in the intermediate layer is stretched during the forming step. In this instance, the intermediate layer may be of a stretched condition from the beginning. Then, the stretch rate of the film in the intermediate layer can be increased during the forming to thereby improve the gas barrier property further.

10 In the forming step, the temperature may be such that the inner and outer layers are brought into a molten condition and the intermediate layer into a softened condition. In providing the rigid layer, a surface layer of a thermoplastic resin may simultaneously be provided outside the rigid layer. The rigid layer and the surface layer may be formed simultaneously by extruding the materials for the layers onto the laminated sheet.

15 According to the features of the present invention, the container has a structure including a barrier layer disposed between the inner and outer layers and made of a resin material whose gas barrier property is improved when it is stretched. The barrier layer is in a stretched condition so that it has an improved gas barrier property. The barrier layer which is in a stretched condition has a tendency of shrinking when it is subjected to heat under a high humidity which may be applied during retort sterilization; however, since the 20 inner and outer layers are not in a stretched condition, they are not distorted even under such condition. It is therefore possible to prevent the shrinkage of the barrier layer and the barrier layer can be maintained in a highly stretched condition. As the result, it is possible to provide the gas barrier layer with an improved gas barrier property. Further, it is possible to prevent thermal deformation of the container.

25 According to the method of the present invention, there is first provided a laminated sheet including an inner and outer layers both made of a thermoplastic resin and an intermediate layer disposed between the inner and outer layers and made of a resin material whose gas barrier property can be improved by stretching and the laminated sheet is then formed into a desired shape under a temperature which is higher than the melting temperature of the inner and outer layers but lower than the melting temperature of the intermediate layer. In the forming step, the intermediate layer is subjected to stretching, in which the stretch rate is usually 2 30 to 10. Thus, the gas barrier property of the intermediate layer is improved. In the case where the intermediate layer is in advance stretched, the stretch rate is further increased by the forming and the barrier property is further improved.

35 The rigid layer outside the outer layer can be made of inorganic materials which are of low price. Therefore, an advantage is obtained from the economical point of view as compared with the case where a required rigidity is provided solely by the outer layer. The rigid layer may be made of a mixture of polypropylene, calcium carbide, talc, silica and/or mica. In this case, it is possible to provide a container which will be free from shrinkage under the heat which may be applied to the container during retort sterilization. Further, the con-

tainer of this structure can readily be burnt when it is to be disposed of. It should further be noted that scrap materials may also be used to form the rigid layer. For example, scrap materials may be crushed and mixed with polypropylene and inorganic materials.

The above and other objects and features of the present invention will become apparent from the following description of preferred embodiments described with reference to the accompanying drawings in which:

Figure 1 is a perspective view of a container in accordance with one embodiment of the present invention;

Figure 2 is a sectional view showing the structure of the wall of the container;

Figure 3 is a sectional view showing another example of the wall structure of the container;

Figure 4 is a sectional view showing a further example of the wall structure;

Figure 5 is a sectional view showing a further example of the wall structure;

Figure 6 is a diagrammatical illustration of a heating device; and,

Figure 7 is a diagram showing the temperature responsive property of resin material.

Referring to the drawings, particularly to Figure 1, there is shown a container 1 for foodstuffs which includes a container body 1a made from a sheet by hot pressing and having an annular flange 1b provided around the upper periphery of the body 1a. After the content is charged, a lid (not shown) is attached to the flange 1b by for example heat sealing. Referring to Figure 2, the container 1 is shown as being made of a laminated sheet comprising an inner layer 2, a barrier layer 3 which is located at one side of the inner layer 2 and an outer layer 4 located along the outer side of the barrier layer 3. A rigid layer 5 is located along the outer side of the outer layer 4. The inner layer 2 is made of a polypropylene film having a thickness of 30 to 200  $\mu\text{m}$ . It is preferable that the inner layer 2 is 50 to 150  $\mu\text{m}$  thick. The barrier layer 3 is made of a stretched vinylidene chloride copolymer film of 10 to 150  $\mu\text{m}$  thick, preferably 15 to 100  $\mu\text{m}$  thick. An adhesive layer 6 of polyurethane is provided between the inner layer 2 and the outer layer 3. The outer layer 3 is made of a material similar to that of the inner layer 2 and is 10 to 200  $\mu\text{m}$  thick, preferably 20 to 100  $\mu\text{m}$  thick. There is provided an adhesive layer 7 of polyurethane similar to the layer 6 between the barrier layer 3 and the outer layer 4. The rigid layer 5 is made of a mixture of polypropylene with calcium carbide, talc, silica, mica and the like and has a thickness of 200 to 2000  $\mu\text{m}$ , preferably 300 to 1500  $\mu\text{m}$ .

In manufacture, a laminated sheet comprising the inner layer 2, the barrier layer 3 and the outer layer 4. The rigid layer 5 is then formed outside the outer layer 4 by extruding the aforementioned mixture in a molten form. Thereafter, the laminated sheet with the rigid layer 5 is placed in a mould and press forming is carried out

under a temperature which is higher than the melting point of the material of the inner layer 2 and the outer layer 4 but lower than the melting point of the material of the barrier layer 3. In this forming step, the vinylidene chloride copolymer film constituting the barrier layer 3 is stretched with a stretching rate of 2 to 10. By this stretching, the barrier layer possesses an improved gas barrier property. If a higher gas barrier property is required, a stretched film may be used for the barrier layer 3 in providing the laminated sheet. If for example a biaxial stretched film of a stretch rate of approximately 5 is used for providing the laminated sheet, it is possible to obtain a higher stretch rate so that a further improved gas barrier property will be obtained.

5 Polypropylene has a melting point of 140 to 160  $^{\circ}\text{C}$  whereas vinylidene chloride copolymer has a melting point of 160  $^{\circ}\text{C}$ . It will therefore be noted that in the case where vinylidene chloride copolymer of non-stretched form is used for the barrier layer 3 in forming the laminated sheet, it is required to select polypropylene having a relatively low melting point. Vinylidene chloride copolymer in a stretched condition has a melting point of approximately 170  $^{\circ}\text{C}$ , so that the melting point of the barrier layer can always be higher than the melting point of the inner and outer layers.

10 The container 1 thus formed has a gas barrier layer 3 made of a stretched film. Therefore, it has an excellent gas barrier property and is suitable for storing its content for a prolonged period of time. Since the inner and outer layers are of non-stretched resin, it is unlikely that the container will be deformed by the heat to which the container may be subjected after the forming process. It should therefore be understood that even when the container is subjected to a retort sterilization after the container is charged with its content and sealed, it is unlikely that the container will be deformed under the heat to which the container is subjected during the sterilization. Further, the barrier layer 3 can be maintained in a stretched condition even after the sterilization. For 15 the purpose of maintaining the shape of the container, the rigid layer 5 may not be necessary if the outer layer 4 is sufficiently thick. However, from the viewpoint of economy, it is preferable to make the outer layer 4 as thin as possible and to provide the shape maintaining ability by the rigid layer 5.

20 Referring to Figure 3, there is shown another embodiment of the present invention. In this embodiment, the laminated sheet includes an inner layer 12 made of a polyolefin film and the barrier layer outside the inner layer 12 is constituted by a first barrier layer 13 adjacent to the inner layer 12 and a second barrier layer located outside the first barrier layer 13a. The first barrier layer 13 is made of a stretched film of vinylidene chloride copolymer and the second barrier layer 13a is made of a stretched film of ethylene-vinyl alcohol copolymer. The first barrier layer 13 and the second barrier layer 13a may be of a stretched form when it is incorporated into the laminated sheet. Then, the stretch rate will be increased during the forming step. If films of non-

stretched form are used as the first and second barrier layers in providing the laminated sheet, the films are stretched only through the forming step. The outer layer is made of a film of polyolefin and the rigid layer 15 is made of a mixture of polyolefin and inorganic material. In the case where polypropylene is used as the polyolefin, the melting point is 140 to 160 °C as already mentioned. Where polyethylene is used, its melting point is 120 to 130 °C. Since ethylene-vinyl alcohol copolymer has melting point of 170 to 190 °C, there will be no problem in controlling the temperature conditions. Stretched ethylene-vinyl alcohol copolymer constituting the second barrier layer 13a has a gas barrier property; however, the gas barrier property will be decreased when it is exposed to an atmosphere of high temperature and high humidity, which may be the atmosphere of a retort sterilizing process. However, even if the gas barrier property is once decreased, the stretched ethylene-vinyl alcohol copolymer can restore the gas barrier property when it is dried. It is preferable to locate the stretched ethylene-vinyl alcohol copolymer film layer 13a outside the first barrier layer 13 so that the layer 13a can be readily dried after the retort sterilization process. The stretched vinylidene chloride copolymer film can be located at an inner side where drying can hardly proceed since there will be no decrease in the gas barrier property.

Figure 4 shows a further embodiment of the present invention which includes, as in the embodiment of Figure 1, an inner layer 2, a barrier layer 3 and an outer layer 4 which are bonded together by means of adhesive layers 6 and 7. A rigid layer 5 is located outside the outer layer 4. The inner layer 2 and the outer layer 4 are made of polyolefin. The barrier layer 3 is made of a film of stretched vinylidene chloride copolymer. The rigid layer 5 is made of a mixture of polyolefin and inorganic material. In this embodiment, there is a layer 8 made of a film of stretched ethylene-vinyl alcohol copolymer which is located outside the rigid layer 5. Outside the layer 8, there is a protective layer 9 made of a mixture of polyolefin and inorganic material.

The layers 5, 8 and 9 can be made by a simultaneous extrusion of resin materials in molten form. With this extrusion process, the layer 8 of ethylene-vinyl alcohol copolymer will be of a non-stretched form; however, it will be stretched during the forming process. When it is desired to increase the stretch rate of the layer 8, the layer 5 may at first be formed over the laminated sheet comprising the layers 2, 3 and 4 by extruding the material in a molten state, and a stretched film of ethylene-vinyl alcohol copolymer is then adhesively attached to the rigid layer 5. Thereafter, the layer 9 is formed by an extrusion process. The stretch rate of the film constituting the layer 8 can further be increased when the sheet is formed into the container 1.

Description will now be made on the case where the melting point of the material for the inner layer and the outer layer and that of the material for the barrier layer are substantially the same or the melting point of

the material for the inner and outer layer is to a certain degree lower than that of the material for the barrier layer. In this instance, the laminated sheet includes as shown in Figure 5 an inner layer 22, a barrier layer 23 attached through an adhesive layer 26 to the outer surface of the inner layer 22 and an outer layer 24 attached through an adhesive layer 27 to the outer surface of the barrier layer 23. A rigid layer 25 is formed outside the outer layer 24 and a surface layer 28 is formed outside the rigid layer 25. The inner layer 22 is made of polypropylene resin and is 70 µm thick. The outer layer 24 is similarly made of polypropylene resin and is 30 µm thick. The barrier layer 23 is made of a non-stretched film of vinylidene chloride-acrylic acid ester copolymer having a softening point of 120 °C and a melting point of 160 °C and has a thickness of 50 µm. Polyurethane adhesive is used for the adhesive layers 26 and 27. The rigid layer 25 is made of a mixture of polypropylene and 30 wt % of talc and has a thickness of 1000 µm. The surface layer 28 is provided to coat the surface of the rigid layer 25 to improve the appearance and the printing property. The layer 28 may be made of polypropylene and is 50 µm thick.

Referring to Figure 6, there is shown a process for heating the sheet as shown in Figure 5. In the process, use is made of a heating apparatus including an upper heater 30 and a lower heater 31. The upper heater 30 may include six heating elements of 300 watts which are arranged in a square frame of 0.5 m long at each side. The lower heater 31 may include nine heating elements of 300 watts arranged in a similar manner as in the case of the upper heater. In the heating apparatus thus constructed, the laminated sheet 32 is placed with the inner layer 22 laid at the upper side and a heating step is carried out. The heating process is carried out so that the heating time for the inner layer side is 12 seconds and the heating time for the surface layer side is 24 seconds. The temperature of the laminated sheet 32 is then measured. It was found that the temperature of the surface of the inner layer is 165 °C and the temperature of the surface of the surface layer 28 was 170 °C, whereas the temperature of the inner layer 22 at the surface facing the adhesive layer 26 is 150 °C and the temperature of the outer layer 24 at the side of the adhesive layer 27 was also 150 °C. It will be noted that by carrying out a forming process with this temperature condition, it is possible to stretch the resin in the barrier layer 23. In a test with an actual example, a formed container was charged with hot water and a closure was attached by heat sealing. Thereafter, the container was subjected to a retort sterilization process at 125 °C for 30 minutes. It has been found that there was no change in the container and the gas barrier property was improved so as to be two times better than the estimated value in the case where a non-stretched layer is used.

A similar test was made with an example in which the barrier layer 23 was made of a biaxially stretched film of vinylidene chloride-acrylic acid ester copolymer having a melting point of 170 °C and a thickness of 50

μm. It was found that the gas barrier property was further improved.

Figure 7 is a diagram showing a typical example of the temperature responsive characteristics of polypropylene resin. In the diagram, the point A on the solid line shows the Vicat softening point whereas the point B shows the melting point. It is preferable to conduct the forming process so as to produce stretching in the shadowed area C between the Vicat softening point A and the melting point B. It is further preferable that the forming process does not produce stretching at a temperature region D which is higher than the melting point B. In the case where the melting temperature of the material for the inner layer and the outer layer and the melting temperature of the material for the barrier layer are substantially the same, the heating process may be controlled so that the temperature at the boundaries of the inner and outer layers and the barrier layer is slightly lower than the melting point. Then, the substantial part of the inner and outer layers will be brought into a molten condition whereas the barrier layer will be maintained at a softened state. Therefore, it is possible to apply an adequate stretching to the barrier layer. It will be noted in Figure 7 that in the case where the barrier layer is made of a resin material having a melting point which is higher than that of the material for the inner and outer layers, the temperature characteristics of the barrier layer will be as shown by a broken line in Figure 7 with respect to the characteristics of the resin material for the inner and outer layers so that the heating control will become easier. In any event, the control of heat energy in a unit of time and the overall heat energy should be determined taking into account the thickness of each layer and the thermal conductivity of the resin material constituting each layer so that a desired temperature gradient can be obtained.

The laminated structure as shown in Figure 5 can of course be used for the forming process as described with reference to the structures of Figures 1 through 4.

#### Claims

1. A container including

an inner layer and an outer layer each made of a thermoplastic material selected from polypropylene resin, high density polyethylene resin, polyethylene-terephthalate resin, polycarbonate resin and polymethyl pentene resin, and

a barrier layer disposed between said inner and outer layers and made of a resin material, selected from vinylidene chloride copolymer, ethylene-vinyl alcohol copolymer, polybutylene-terephthalate, acrylonitrile copolymer, nylon-6, metaxylenediamine, and condensed adipic acid copolymer,

said barrier layer being held between the inner and outer layers with the resin material constituting the barrier layer being in a stretched condi-

tion and the thermoplastic material of said inner and outer layers being in a non-stretched condition.

- 5 2. A container in accordance with claim 1 which includes a rigid layer of a thickness larger than the total thickness of said inner, outer and barrier layers, provided outside said outer layer.
- 10 3. A container in accordance with claim 1 in which said barrier layer includes a first layer made of stretched vinylidene chloride copolymer and a second layer made of stretched ethylene vinyl alcohol copolymer, said first layer being located at the side adjacent to said inner layer.
- 15 4. A container in accordance with claim 2, in which said rigid layer includes at least one inorganic material.
- 20 5. A container in accordance with claim 4, in which said inner layer is a polypropylene film, in which said barrier layer includes at least one film of stretched vinylidene chloride copolymer; in which said rigid layer is made of a mixture of polypropylene and at least one inorganic material.
- 25 6. A container in accordance with claim 5 which includes a second barrier layer between said at least one film of stretched vinylidene chloride copolymer and said outer layer, said second barrier layer being a film of stretched ethylene-vinyl alcohol copolymer.
- 30 7. A method for manufacturing a container in accordance with claim 1, including the steps of:
  - 35 providing a laminate comprising an inner layer and an outer layer both made of a thermoplastic material and a barrier layer located between the inner and outer layers and made of a resin material having a melting point not lower than the melting point of the material of said inner and outer layers, said resin material of said barrier layer being one whose gas barrier property can be improved by stretching;
  - 40 heating said laminate to a temperature which is higher than the melting point of the material of said inner and outer layers but lower than the melting point of the material of said barrier layer, and
  - 45 forming said laminate into a desired shape so that said barrier layer is stretched during the forming step.
- 50 8. A method in accordance with claim 7 in which a rigid layer of a thickness larger than the thickness of said laminate, is formed outside said outer layer of said laminate prior to the forming step, said rigid layer including an inorganic material.

9. A method in accordance with claim 8 in which said inner layer is a film of polypropylene, said outer layer is a film of polypropylene, and said barrier layer is a film of vinylidene chloride copolymer.

10. A method in accordance with claim 9 in which said film of vinylidene chloride copolymer is a film of stretched vinylidene chloride copolymer, and in which the extent of stretching thereof is increased during the forming step.

11. A method for manufacturing a container in accordance with claim 1, including the steps of:

providing a laminate including at least an inner layer made of a thermoplastic material, an outer material and a barrier layer including at least one resin material whose gas barrier property can be improved by stretching;

heating said laminate at the opposite sides thereof so that said inner and outer layers are brought into a molten condition and said barrier layer is brought into a softened condition; and

forming said laminate into a desired shape so that said barrier layer is stretched during the forming step.

12. A method in accordance with claim 11 in which said barrier layer is made of a biaxially stretched resin film.

13. A method in accordance with claim 11 in which said heating step is controlled in respect of heat energy applied in a unit of time and overall heat energy applied during the heating step so that said inner and outer layers are brought into a molten condition and said barrier layer is brought into a softened condition due to a temperature gradient through the thickness of said inner and outer layers.

14. A method in accordance with claim 11 in which said laminate includes a rigid layer, of a thickness larger than the total thickness of said inner, outer and barrier layers, which is located outside said outer layer, said rigid layer being made of a mixture of a thermoplastic material and at least one inorganic material.

15. A method in accordance with claim 11 in which said inner and outer layers and said barrier layer are adhesively attached together, in which a mixture of a thermoplastic material and at least one inorganic material is extruded in a molten state onto an outer surface of said outer layer to provide a rigid layer, and in which a molten thermoplastic material is extruded onto said rigid layer to form a surface layer thereby to provide a container blank; said container blank then being heated so that said inner and outer layers are brought into a substantially molten condition and said barrier layer is brought into a soft-

tened condition, and said container blank then being formed into a desired shape.

5 16. A method in accordance with claim 15 in which said mixture for forming said rigid layer and said thermoplastic material for forming said surface layer are extruded simultaneously.

#### Patentansprüche

1. Behälter, umfassend eine Innenschicht und eine Außenschicht, jeweils hergestellt aus einem thermoplastischen Material, gewählt aus Polypropylenharz, Polyethylenharz hoher Dichte, Polyethylenterephthalatharz, Polycarbonatharz und Polmethylpentenharz, und eine Barrièreschicht, eingebracht zwischen die Innenschicht und die Außenschicht und hergestellt aus einem Kunststoff, gewählt aus Vinylidenchlorid-Copolymer, Ethylen-Vinylalkohol-Copolymer, Polybutylen-Terephthalat, Acrylnitril-Copolymer, Nylon-6, Metaxylendiamin und kondensiertem Adipinsäure-Copolymer, worin die Barrièreschicht zwischen der Innenschicht und der Außenschicht gehalten wird, indem der Kunststoff, welcher die Barrièreschicht bildet, in gerecktem Zustand und das thermoplastische Material der Innenschicht und Außenschichten in nicht-gerecktem Zustand vorliegen.
2. Behälter nach Anspruch 1, welcher eine starre Schicht einer Dicke von mehr als der Gesamtdicke von Innenschicht, Außenschicht und Barrièreschicht enthält, die an der Außenseite der Außenschicht angebracht ist.
3. Behälter nach Anspruch 1, bei dem die Barrièreschicht eine erste Schicht, hergestellt aus gerecktem Vinylidenchlorid-Copolymer, und eine zweite Schicht umfaßt, hergestellt aus gerecktem Ethylen-Vinylalkohol-Copolymer, wobei diese erste Schicht an der an die Innenschicht angrenzenden Seite angebracht ist.
4. Behälter nach Anspruch 2, in welchem die starre Schicht mindestens einen anorganischen Stoff umfaßt.
5. Behälter nach Anspruch 4, in welchem die Innenschicht ein Polypropylenfilm ist; in welchem die Barrièreschicht mindestens einen Film aus gerecktem Vinylidenchlorid-Copolymer enthält; in welchem die starre Schicht aus einem Gemisch von Polypropylen und mindestens einem anorganischen Stoff hergestellt ist.
6. Behälter nach Anspruch 5, welcher eine zweite Barrièreschicht zwischen diesem mindestens einem Film aus gerecktem Vinylidenchlorid-Copo-

lymer und dieser Außenschicht enthält, wobei diese zweite Barrièreschicht ein Film aus gerektem Ethylen-Vinylalkohol-Copolymer ist.

7. Verfahren zur Herstellung eines Behälters nach Anspruch 1, umfassend die folgenden Schritte: Bereitstellen eines Laminats, umfassend eine Innenschicht und eine Außenschicht, beide hergestellt aus einem thermoplastischen Material, und eine Barrièreschicht, die eingebracht zwischen die Innen- und die Außenschicht und hergestellt aus einem Kunststoff mit einem nicht geringeren Schmelzpunkt als der Schmelzpunkt des Materials der Innen- und Außenschichten ist, wobei der Kunststoff der Barrièreschicht ein solcher ist, dessen Gasbarriere-Eigenschaft durch Recken verbessert werden kann;  
Erhitzen des Laminats auf eine Temperatur, die höher ist als der Schmelzpunkt des Materials der Innen- und Außenschichten, aber niedriger als der Schmelzpunkt des Materials der Barrièreschicht, und  
Formen des Laminats zu gewünschter Gestalt, so daß die Barrièreschicht während des Formschritts gereckt ist.

8. Verfahren nach Anspruch 7, worin eine starre Schicht einer Dicke von mehr als der Dicke des Laminats auf der Außenseite der Außenschicht des Laminats vor dem Formschritt gebildet wird, wobei die starre Schicht einen anorganischen Stoff enthält.

9. Verfahren nach Anspruch 8, worin die Innenschicht ein Film aus Polypropylen ist, die Außenschicht ein Film aus Polypropylen ist und die Barrièreschicht ein Film aus Vinylidenchlorid-Copolymer ist.

10. Verfahren nach Anspruch 9, worin der Film aus Vinylidenchlorid-Copolymer ein Film aus gerektem Vinylidenchlorid-Copolymer ist und worin der Grad seiner Reckung während des Formschritts erhöht wird.

11. Verfahren zur Herstellung eines Behälters nach Anspruch 1, umfassend die folgenden Schritte: Bereitstellen eines Laminats, umfassend mindestens eine Innenschicht aus einem thermoplastischen Material, ein Außenmaterial und eine Barrièreschicht, umfassend mindestens einen Kunststoff, dessen Gasbarriere-Eigenschaft sich durch Recken verbessern läßt;  
Erhitzen des Laminats an den entgegengesetzten Seiten davon, so daß die Innen- und Außenschichten in einen geschmolzenen Zustand gebracht werden und die Barrièreschicht in einen erweichten Zustand gebracht wird; und  
Formen des Laminats zu gewünschter Gestalt, so daß die Barrièreschicht während des Formschritts gereckt ist.

12. Verfahren nach Anspruch 11, worin die Barrièreschicht aus einem biaxial gereckten Kunststofffilm hergestellt ist.

13. Verfahren nach Anspruch 11, worin der Erhitzungsschritt hinsichtlich der zugeführten Wärmeenergie in einer Zeiteinheit und der zugeführten Gesamt-wärmeenergie während des Erhitzungsschritts kontrolliert ist, so daß die Innen- und Außenschichten in einen geschmolzenen Zustand gebracht werden und die Barrièreschicht in einen erweichten Zustand aufgrund eines Temperaturgradienten durch die Dicke der Innen- und Außenschichten gebracht wird.

14. Verfahren nach Anspruch 11, worin das Laminat eine starre Schicht einer Dicke von mehr als der Gesamtdicke der Innen-, Außen- und Barrièreschichten enthält, die an der Außenseite dieser Außenschicht angebracht ist, wobei die starre Schicht aus einem Gemisch aus einem thermoplastischen Material und mindestens einem anorganischen Stoff hergestellt ist.

15. Verfahren nach Anspruch 11, worin die Innen- und Außenschichten und die Barrièreschicht aneinander gebunden werden, worin ein Gemisch eines thermoplastischen Materials und mindestens eines anorganischen Materials in einem geschmolzenen Zustand auf die Außenseite der Außenschicht extrudiert wird, um eine starre Schicht bereitzustellen, und worin ein geschmolzenes thermoplastisches Material auf die starre Schicht zur Bildung einer Oberflächenschicht extrudiert wird, um dadurch einen Behälterrohling zu erhalten; wobei dieser Behälter.... dann so erhitzt wird, daß die Innen- und Außenschichten in einen im wesentlichen geschmolzenen Zustand gebracht werden und die Barrièreschicht in einen erweichten Zustand gebracht wird, und dieser Behälterrohling dann zu gewünschter Gestalt geformt wird.

16. Verfahren nach Anspruch 15, worin das Gemisch zur Bildung der starren Schicht und das thermoplastische Material zur Bildung der Oberflächenschicht gleichzeitig extrudiert werden.

#### Revendications

1. Récipient comprenant :  
une couche interne et une couche externe, chacune constituée par un matériau thermoplastique choisi parmi les résine polypropylène, résine polyéthylène haute densité, résine poly(éthylène téréphthalate), résine polycarbonate et résine polyméthylpentène, et

une couche barrière disposée entre lesdites couches interne et externe, et constituée par un matériau résineux choisi parmi les copolymère de chlorure de vinylidène, copolymère éthylène/(alcool de vinyle), poly(butylène téréphthalate), copolymère d'acrylonitrile, nylon-6, métaxylénediamine et copolymère d'acide adipique condensé, 5

ladite couche barrière étant maintenue entre les couches interne et externe, et le matériau résineux, qui constitue la couche barrière, étant dans un état étiré, et le matériau thermoplastique desdites couches interne et externe étant dans un état non-étiré. 10

2. Récipient conforme à la revendication 1, qui comprend une couche rigide présentant une épaisseur plus grande que l'épaisseur totale desdites couches interne, externe et barrière, et formée à l'extérieur de ladite couche externe. 15

3. Récipient conforme à la revendication 1, dans lequel ladite couche barrière comprend une première couche constituée par un copolymère de chlorure de vinylidène étiré et une seconde couche constituée par un copolymère éthylène/(alcool de vinyle) étiré, ladite première couche étant située sur le côté adjacent à ladite couche interne. 20

4. Récipient conforme à la revendication 2, dans lequel ladite couche rigide comprend au moins un matériau minéral. 25

5. Récipient conforme à la revendication 4, dans lequel ladite couche interne est un film de polypropylène, dans lequel ladite couche barrière comprend au moins un film de copolymère de chlorure de vinylidène étiré ; dans lequel ladite couche rigide est constitué par un mélange de polypropylène et d'au moins un matériau minéral. 30

6. Récipient conforme à la revendication 5, qui comprend une seconde couche barrière entre ledit film de copolymère de chlorure de vinylidène étiré au nombre d'au moins un et ladite couche externe, ladite seconde couche barrière étant un film de copolymère éthylène/(alcool de vinyle) étiré. 35

7. Procédé de fabrication d'un récipient conforme à la revendication 1, comprenant les étapes de : 40

formation d'un stratifié qui comprend une couche interne et une couche externe, constituées toutes les deux par un matériau thermoplastique, et une couche barrière située entre les couches interne et externe et constituée par un matériau résineux qui présente un point de fusion qui n'est pas inférieur au point de fusion du matériau desdites couches interne et externe, ledit matériau résineux de ladite couche barrière étant un matériau dont on peut améliorer la propriété de barrière aux 45

gaz par étirage ; 50

chauffage dudit stratifié à une température qui est supérieure au point de fusion du matériau desdites couches interne et externe, mais inférieur au point de fusion du matériau de ladite couche barrière, et

façonnage dudit stratifié sous une forme voulue pour que ladite couche barrière soit étirée au cours de l'étape de façonnage. 55

8. Procédé conforme à la revendication 7, dans lequel on forme une couche rigide, présentant une épaisseur plus grande que l'épaisseur dudit stratifié, sur la face extérieure de ladite couche externe dudit stratifié avant l'étape de façonnage, ladite couche rigide comprenant un matériau minéral.

9. Procédé conforme à la revendication 8, dans lequel ladite couche interne est un film de polypropylène, ladite couche externe est un film de polypropylène, et ladite couche barrière est un film de copolymère de chlorure de vinylidène.

10. Procédé conforme à la revendication 9, dans lequel ledit film de copolymère de chlorure de vinylidène est un film de copolymère de chlorure de vinylidène étiré, et dans lequel le taux d'étirage est augmenté au cours de l'étape de façonnage.

11. Procédé de fabrication d'un récipient conforme à la revendication 1, comprenant les étapes de : 60

formation d'un stratifié qui comprend au moins une couche interne constituée par un matériau thermoplastique, un matériau externe et une couche barrière comprenant au moins un matériau résineux dont la propriété de barrière aux gaz peut être améliorée par étirage ;

chauffage dudit stratifié sur ses faces opposées pour que lesdites couches interne et externe soient amenées dans un état de fusion et ladite couche barrière soit amenée dans un état de ramollissement ; et 65

façonnage dudit stratifié sous une forme voulue pour que la couche barrière soit étirée au cours de l'étape de façonnage.

12. Procédé conforme à la revendication 11, dans lequel ladite couche barrière est constituée par un film de résine étiré biaxialement.

13. Procédé conforme à la revendication 11, dans lequel on règle ladite étape de chauffage suivant l'énergie thermique appliquée dans un intervalle de temps et l'énergie thermique globale appliquée au cours de l'étape de chauffage pour que lesdites couches interne et externe soient amenées dans un état de fusion et que ladite couche barrière soit amenée dans un état de ramollissement en raison

d'un gradient de température à travers l'épaisseur desdites couches interne et externe.

14. Procédé conforme à la revendication 11, dans lequel ledit stratifié comprend une couche rigide, présentant une épaisseur plus grande que l'épaisseur totale desdites couches interne, externe et barrière, qui est située à l'extérieur de ladite couche externe, ladite couche rigide étant constituée par un mélange d'un matériau thermoplastique et d'au moins un matériau minéral. 10

15. Procédé conforme à la revendication 11, dans lequel lesdites couches interne et externe et ladite couche barrière sont liées ensemble de manière adhésive, dans lequel un mélange d'un matériau thermoplastique et d'au moins un matériau minéral est extrudé à l'état fondu sur une surface externe de ladite couche externe pour former une couche rigide, et dans lequel un matériau thermoplastique fondu est extrudé sur ladite couche rigide pour former une couche de surface, ce qui donne une ébauche de récipient ; ladite ébauche de récipient étant ensuite chauffée pour que lesdites couches externe et interne soient amenées dans un état de quasifusion et que ladite couche barrière soit amenée dans un état de ramollissement, et ladite ébauche de récipient étant ensuite façonnée sous une forme voulue. 20 25

16. Procédé conforme à la revendication 15, dans lequel ledit mélange pour former ladite couche rigide et ledit matériau thermoplastique pour former ladite couche de surface sont extrudées simultanément. 30 35

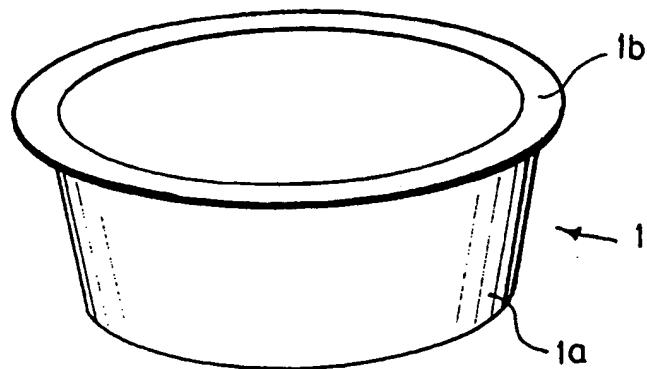
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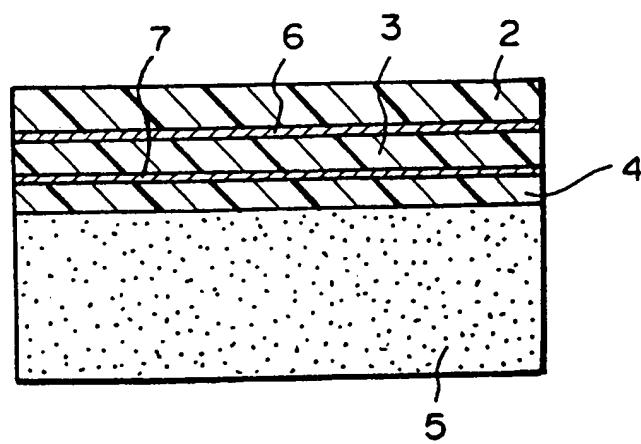
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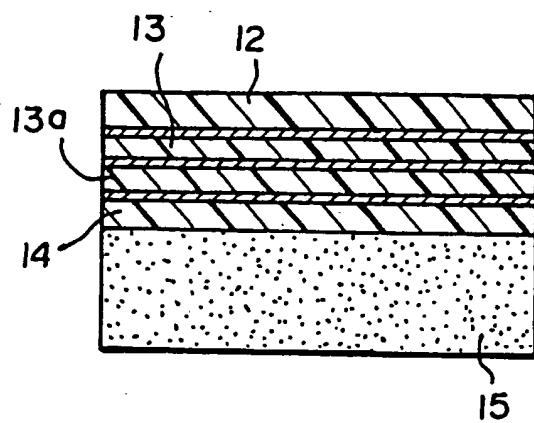
**FIG. 1**



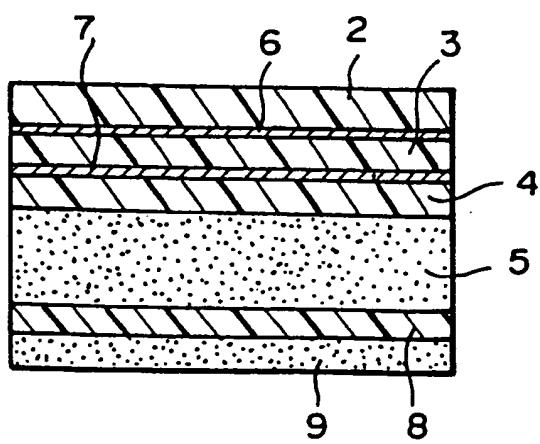
**FIG. 2**



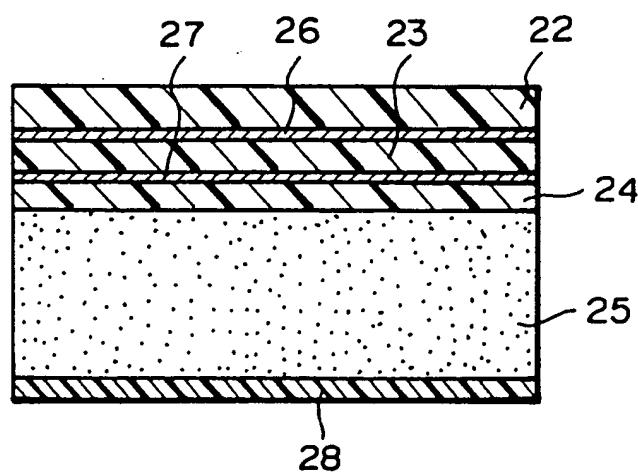
**FIG. 3**



**FIG. 4**



**FIG. 5**



**FIG. 6**

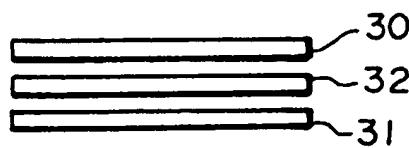


FIG. 7

